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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>4</sup> :</b> C08J 9/32, C08L 63/00 H01Q 15/14, C08K 7/00	<b>A1</b>	<b>(11) International Publication Number:</b> WO 85/ 05113 <b>(43) International Publication Date:</b> 21 November 1985 (21.11.85)
<b>(21) International Application Number:</b> PCT/US85/00625 <b>(22) International Filing Date:</b> 9 April 1985 (09.04.85) <b>(31) Priority Application Numbers:</b> 607,847 609,178 <b>(32) Priority Dates:</b> 7 May 1984 (07.05.84) 11 May 1984 (11.05.84) <b>(33) Priority Country:</b> US <b>(71) Applicant:</b> HUGHES AIRCRAFT COMPANY [US/ US]; 200 North Sepulveda Boulevard, El Segundo, CA 90245 (US). <b>(72) Inventors:</b> DuPONT, Preston, S. ; 9046 Bertrand Ave- nue, Northridge, CA 91325 (US). FREEMAN, Janet, E. ; 129 North Bonnie Avenue #1, Pasadena, CA 91106 (US). RITTER, Robert, E. ; 741 Cloyden Road, Palos Verdes Estates, CA 90274 (US). WITTMANN, Alois ; 29017 Geronimo Drive, Palos Verdes, CA 90274 (US). OLDHAM, Susan, L.; 3472 Heather Road, Long Beach, CA 90808 (US).		<b>(74) Agents:</b> LACHMAN, Mary, E. et al.; Hughes Aircraft Company, Post Office Box 1042, Bldg. C2, M.S. A126, El Segundo, CA 90245 (US). <b>(81) Designated States:</b> AU, DE (European patent), FR (Eu- ropean patent), GB (European patent), IT (European patent), JP, SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FIBER-REINFORCED SYNTACTIC FOAM COMPOSITES AND METHOD OF FORMING SAME  <b>(57) Abstract</b>  Fiber-reinforced syntactic foam composites having a low specific gravity and a low coefficient of thermal expansion suitable for forming lightweight structures for spacecraft applications are prepared from a mixture of a heat curable thermosetting resin, hollow microspheres having a diameter of about 5 to 200 micrometers and fibers having a length less than or equal to 250 micrometers.		

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FIBER-REINFORCED SYNTACTIC  
FOAM COMPOSITES  
AND METHOD OF FORMING SAME

1

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates, in general, to syntactic foam composites and, more particularly, to fiber-reinforced thermosetting resin based syntactic foam composites exhibiting a low specific gravity and a low coefficient of thermal expansion.

10 2. Description of the Prior Art

A continuing objective in the development of satellites is to optimize satellite payload weight. One means of achieving this objective is to reduce the intrinsic weight of various operational elements within the spacecraft. It has been recognized by the art that the desired weight reduction could be realized by replacing conventional materials, such as aluminum, with lower density synthetic composites possessing requisite mechanical, thermal and chemical stability. 15 Included in these low density synthetic composites is a group of materials referred to in the art as syntactic foams. 20

1 can be achieved, as well as reducing dimensional  
stability. If syntactic foam systems are too highly  
filled, sacrifices are made in moldability, coefficient  
of thermal expansion, strength, density, dimensional  
5 stability and stiffness. Moreover, such foams tend to  
exhibit poor adhesion to metallic plating which is  
required to form the desired product, such as an antenna  
component.

10 In order for the syntactic foam to be useful  
as a substitute for aluminum in antenna and antenna  
microwave components in a spacecraft, the foam must  
have the following characteristics.

15 (1) The material must have a specific gravity  
of 1.00 or less, as compared to a specific gravity  
of 2.7 for aluminum.

(2) The material must have a linear coeffi-  
cient of thermal expansion ( $\alpha$  or CTE) comparable  
to that of aluminum, preferably close to  
13 x 10<sup>-6</sup> in/in/°F (23 x 10<sup>-6</sup> cm/cm/°C) or less.  
20 Thermal distortion of antenna components subjected  
to thermal cycling in the extremes of the space  
environment is a major contributing factor to  
gain loss, pointing errors, and phase shifts.

25 (3) The material must meet the National  
Aeronautics and Space Administration (NASA)  
outgassing requirements to insure that the  
material does not release gaseous component  
substances which undesirably accumulate on other  
spacecraft parts in the outer-space vacuum.

30 (4) The material must have long-term  
stability, as required for parts exposed to the  
space temperature environment (e.g., -100°F to  
250°F or -73°C to 121°C) for extended periods of  
time, such as 10 years.

1 bonded together by the heat cured resin matrix. The  
composites of the present invention readily meet the  
specific gravity, coefficient of thermal expansion and  
NASA outgassing requirements, which easily qualify the  
5 composites as aluminum substitutes for spacecraft use.

#### DETAILED DESCRIPTION OF THE INVENTION

10 In order to form the fiber-resin-microsphere  
composite of the present invention having the desired  
density and coefficient of thermal expansion, each of  
the three components must be selected so that the  
resulting combination thereof provides a mixture amenable  
to being cast into the desired configuration, as well  
as providing a final product having the required  
15 structural and physical properties. Acceptable mixtures  
must have a viscosity that produces an accurate, void-  
free casting with uniform material properties. In  
addition, the proportion of fiber in the composite must  
provide the required thermal expansion, strength, and  
20 stiffness properties. Further, the microsphere component  
must be chosen to provide the required low density in  
the composite. Finally, each of the components must be  
capable of being combined with the other components and  
the effect of each on the other in the mixture thereof,  
25 as well as in the final composite must be taken into  
account. In particular the properties of the composite  
are influenced by the properties, relative volume  
ratios, and interactions of the individual components.  
More specifically, density, strength, stiffness  
30 (brittleness), coefficient of thermal expansion and  
processibility are strong functions of filler and fiber  
type, volume ratios and micropacking. The following  
discussion provides a more detailed consideration of  
these various factors. It should be noted that in the

1 practice of the present invention are epoxy resins  
having 1,2 epoxy groups or mixtures of such resins,  
and include cycloaliphatic epoxy resins such as the  
glycidyl ethers of polyphenols, liquid Bisphenol-A  
5 diglycidyl ether epoxy resins (such as those sold  
under the trademarks Epon 815, Epon 825, Epon 828 by  
Shell Chemical Company), phenolformaldehyde novolac  
polyglycidyl ether epoxy resins (such as those sold  
under the trademarks DEN 431, DEN 438 and DEN 439 by  
10 Dow Chemical Company), and epoxy cresol novolacs (such  
as those sold under the trademarks ECN 1235, ECN 1273,  
ECN 1280 and ECN 1299 by Ciba Products Company).

The particular epoxy resins preferred in the  
practice of the present invention are polyglycidyl  
15 aromatic amines, i.e. N-glycidyl amino compounds prepared  
by reacting a halohydrin such as epichlorohydrin with  
an amine. Examples of the most preferred polyglycidyl  
aromatic amines include diglycidylaniline, diglycidyl  
orthotoluidine, tetraglycidyl ether of methylene dianiline  
20 and tetraglycidyl metaxylene diamine, or mixtures  
thereof.

The epoxy resins which are preferably in liquid  
form at room temperature are admixed with polyfunctional  
curing agents to provide heat curable epoxy resins  
25 which are cross-linkable at a moderate temperature,  
e.g., about 100°C, to form thermoset articles. Suitable  
polyfunctional curing agents for epoxy resins include  
aliphatic polyamines of which diethylene triamine and  
triethylene tetramine are exemplary; aromatic amines of  
30 which methylene dianiline, meta phenylene diamine,  
4,4' diaminodiphenyl sulfone are exemplary; and  
polycarboxylic acid anhydrides of which pyromellitic  
dianhydride, benzophenone tetracarboxylic dianhydride,  
hexahydrophthalic anhydride, nadic methyl anhydride  
35 (maleic anhydride adduct of methyl cyclopentadiene),

1           A particularly useful resin composition for  
forming the composites of the present invention comprises  
a polyglycidyl aromatic amine, a polycarboxylic acid  
anhydride curing agent, and a curing accelerator.  
5       Examples 3 and 4 herein are directed to the use of  
this preferred resin formulation in the practice of  
the present invention.

## 2. Hollow Microspheres

10           The syntactic foam composites prepared in accordance  
with the present invention contain a relatively uniform  
distribution of hollow microspheres. These hollow  
microspheres are usually hollow thermoplastic spheres  
composed of acrylic-type resins such as polymethyl-  
15       methacrylate, acrylic modified styrene, polyvinylidene  
chloride or copolymers of styrene and methyl methacrylate;  
phenolic resins; or hollow glass, silica or carbon spheres  
that are very light in weight and act as a lightweight  
filler in the syntactic foam. These microspheres  
20       preferably have a diameter in the range of about 5 to  
about 200 micrometers. Methods for the production of  
these hollow microspheres are well known in the art  
and are discussed, for example, by Harry S. Katz and  
John V. Milewski in the book entitled, "Handbook of  
25       Fillers and Reinforcements for Plastics," Chapter 19:  
Hollow Spherical Fillers, Van Nostrand Reinhold, 1978,  
the teachings of which are incorporated herein by  
reference. Such microspheres are readily available  
commercially. These hollow microspheres can be  
30       compressed somewhat when subjected to external pressure.

1 "Carbosphere" carbon microspheres available from the  
Versar Corporation have a specific gravity of 0.32 and  
a mean diameter of 50 micrometers. Desirably, a mixture  
of two or more types of hollow microspheres may be  
5 employed in the practice of the present invention. The  
glass microspheres provide the syntactic foam with  
improved structural strength, while those of carbon  
advantageously contribute to both a lowered coefficient  
of thermal expansion and greater amenability to subsequent  
10 metal-plating operations. When using a combination of  
glass and carbon microspheres in preparing the composites  
of the present invention, the ratio of glass microspheres  
to carbon microspheres is about 1:4 to 1:1.

Furthermore, it has been found by using packing  
15 theory that an increased volume percent solids in the  
resin mixture can be achieved. Packing theory is based  
on the concept that, since the largest particle size  
filler in a particular reinforcement system packs to  
produce the gross volume of the system, the addition of  
20 succeeding smaller particles can be done in such a  
way as to simply occupy the voids between the larger  
filler without expanding the total volume. This theory  
is discussed by Harry S. Katz and John V. Milewski, in  
the book entitled "Handbook of Fillers and Reinforcements  
25 for Plastics," Chapter 4. Packing Concepts in Utilization  
of Filler and Reinforcement Combinations, Van Nostrand  
Reinhold, 1978. The fillers used in the present  
invention are chosen on the basis of particle size,  
shape, and contribution to overall composite properties.  
30 This theory applies to the use of solid particulates as  
well as hollow spheres. Because of the high viscosity  
of such a highly loaded resin, the mixture could not  
flow into the mold without damaging the microspheres.

1 mixture at a given level of viscosity, which provides a  
higher level of reinforcement at that viscosity level  
by shorter fibers. In addition, the use of shorter  
fibers improves the uniformity of the mix. Thus,  
5 fibers useful in the composite of the present invention  
have a length less than or equal to 250 micrometers  
and generally in the range of about 50 to about 250  
micrometers. Fibers having a length about 150 to  
about 250 micrometers were found to provide the best  
10 compromise between viscosity and reinforcement as  
discussed previously. When graphite fiber, the preferred  
fiber material, is used, the diameter of the graphite  
fibers is in the range of about 5 to about 10 micrometers.

Moreover, the interaction of the fibers with the  
15 microspheres discussed previously must be considered.  
It has been determined by micropacking theory, as  
described in Chapter 4 of the book by Katz and Milewski,  
previously referenced, that the optimum ratio of fibers-  
to-spheres varies with the length/diameter ratio ( $L/D$ )  
20 of the fibers and with the ratio of the sphere-diameter  
to the fiber-diameter ( $R$ ). For each value of  $L/D$ ,  
there is one  $R$  value where the packing efficiency is  
zero; and as  $R$  increases or decreases on either side of  
this minimum, packing efficiency increases. It has  
25 been found most desirable in the practice of the present  
invention to use graphite fibers of the micrometer  
lengths discussed above, which have a length to diameter  
ratio ( $L/D$ ) of about 5:1 to about 30:1 and preferably  
about 15:1 to about 30:1, and a sphere-diameter to  
30 fiber-diameter ratio ( $R$ ) of at least about 6:1 and  
preferably about 15:1.

Graphite fibers used in the practice of the  
present invention are selected to have high strength  
and low density. Celanese GY-70 graphite fiber and  
35 Courtaulds HM-S graphite fiber are especially suitable.

1 titanate coupling agent such as di(dioctylpyrophos-  
phato)ethylene titanate (KR238M available from Kenrich  
Petrochemical Company of Bayonne, New Jersey); or  
5 tetra(2,2 diallyloxymethyl-1-butoxy)titanium di(ditridecyl  
phosphite) (KR55 available from Kenrich); or titanium  
di(cumylphenylate) oxyacetate (KR134S available from  
Kenrich); or isopropyl tridodecylbenzenesulfonyl  
(KR9S available from Kenrich). The coupling agents  
10 enable the resin to wet the sphere and fiber surfaces, and  
promote a stronger bond between the resin, microspheres,  
and fibers without increasing the viscosity appreciably.

The coupling agents may be applied by simply  
dissolving the agents in the resin-microsphere-fiber  
blend. Optionally, these agents may be applied by  
15 first dissolving the agents at a concentration of  
0.1 - 0.5% of the filler weight in water or an organic  
solvent such as isopropanol or Freon TE (a fluorocarbon  
compound available from E.I. Dupont and Company); and  
then immersing the microspheres and fibers which have  
20 been premixed in predetermined proportions in the  
solution for a period of 5 to 30 minutes, followed by  
filtering and drying the mixture. The microsphere-fiber  
mixture may then be blended with the heat curable resin  
preparatory to fabricating the syntactic foam composite.

#### 25 4. Optional Microbeads

Solid microbeads may optionally be incorporated  
in the composite of the present invention in order to  
increase packing efficiency. Advantageously, such  
30 microbeads were also found to decrease the viscosity of  
the formulation, improve its pourability, and increase  
composite uniformity. In a preferred practice of the  
present invention, about 2 to about 8 percent by volume  
of solid inert material, such as glass or silica micro-  
35 beads having a diameter of about 2 to about 8 micrometers

1 at which the resin is curable, e.g. to 250°F to 350°F  
(121°C to 177°C), for epoxy resins generally and about  
150°F to 250°F (66 to 121°C) for the preferred epoxy  
composition described herein, at 50 to 100 psi (2586 to  
5 5171 mm Hg or  $7.25$  to  $14.5 \times 10^{-3}$  Pa) for about 2 to  
about 4 hours.

Molding of the filled heat curable resin formula-  
tions to form syntactic foam composites of the present  
invention may also be effected by other conventional  
10 molding methods including transfer molding and compression  
molding procedures wherein the heat curable formulation  
is cured at the above-noted curing temperatures, using  
pressures on the order of 800 to 1000 psi (41372 to 51715  
mm Hg or 0.116 to 0.145 pascals) for 1 to 2 hours.

15 It has been found particularly advantageous to  
form the filled heat curable resin mixtures into the  
syntactic foam composites of the present invention by  
a vacuum liquid transfer molding process. In this  
procedure, the mold is first loaded with the microsphere/  
20 fiber filler which has been mechanically or manually  
premixed in predetermined proportions and pretreated  
with a sizing agent as previously described. Next,  
the mold may optionally be vibrated to promote a  
uniform distribution of the filler in the mold (e.g.  
25 about 5 minutes on a vibration table). Then the mold  
cavity is filled with the heat curable resin. The mold  
is a sealable pressure vessel constructed to support  
the vacuum/pressure sequence described below. To  
prepare for the molding process, the mold cavity is  
30 preheated to bring the cavity up to the temperature at  
which the heat curable resin is curable. A vacuum is  
then drawn on the mold to degas the mold cavity  
contents and to impregnate the filler with the resin.  
The vacuum is released to atmospheric pressure to

1 that of aluminum or steel. Depending on the filler  
fiber volume used in the composite of the present  
invention, composites may be tailored to have coefficients  
of thermal expansion ranging from that of the unfilled  
5 resin to that of steel.

Because of their relatively low coefficient of  
thermal expansion, epoxy resin based syntactic foam  
composites prepared in accordance with the present  
invention have been determined to be especially amenable  
10 to conventional metal plating processes, such as electro-  
less plating, when the surfaces thereof are prepared  
for plating by plasma treatment. The relatively high  
adhesion of metal deposits to the surface of the present  
composite is believed to be a function of both the  
15 topography of the plasma-treated surface plus the  
mechanical integrity of the remaining surface. The  
plasma removes the resin "skin" from the composite,  
leaving the graphite fiber/microballoon filler exposed,  
to provide a surface which is readily platable. Such  
20 metal plating of the composite of the present invention  
may be required in forming antenna components in which  
an electrically conductive surface or path is required,  
as is known in the art.

To effect plasma treatment in preparation for  
25 plating, the surface of the filler reinforced epoxy  
resin based composite is subjected to a plasma process  
with a reaction gas containing a mixture of air, nitrogen,  
or argon with oxygen, water vapor, nitrous oxide, or  
other resin oxidizing source, to remove the polymer  
30 "skin" and expose the filler, as discussed above.  
Normal plasma etching conditions known to the art are  
used. For example, for a plasma excitation energy of  
200 watts/ft<sup>2</sup> of composite, an O<sub>2</sub>/inert gas source  
of approximately 1000 ml/minute, a vacuum pressure of  
35 200 micrometers Hg, and one hour duration are used.

1           Next, a copper plating is built up to any desired  
thickness on the electroless copper by known electrolytic  
plating methods, using commercially available electro-  
deposit copper plating solution. Finally an electrolytic  
5   silver plate is formed to the desired thickness on the  
electrolytic copper plate by known methods, using  
commercially available silver plating solution formula-  
tions. Silver plating of a composite of the present  
invention is described in Example 5.

10           The following examples illustrate but do not limit  
the present invention.

15                   EXAMPLE 1

This example illustrates a process for forming  
one type of fiber-reinforced syntactic foam composite  
in accordance with one process embodiment of the present  
invention.

20           The components of the syntactic foam formulation  
designated "S-61" are shown in Table I. The following  
details regarding the components of S-61 apply to Table I.

- a. MY720 is a tetraglycidyl methylene dianiline  
manufactured by Ciba Geigy.
- 25   b. HY906 is a nadic methyl anhydride hardener  
manufactured by Ciba Geigy.
- c. BDMA is benzyldimethylamine accelerator  
available from E.V. Roberts or Ciba Geigy.
- d. D32/4500 microspheres are borosilicate  
30   microspheres having a mean diameter of 75  
micrometers, a specific gravity of 0.32, and a  
compressive strength of 4500 psi, available from  
the 3M Company.

### Preparation of Graphite Fibers

1           The GY70 graphite fibers in continuous tow form  
were cut into lengths of approximately 1/8 inch to 1/2  
inch (0.32 to 1.27 centimeters), using a paper cutter.  
5       Batches of the chopped fibers (approximately 80 grams  
each) were loaded into a ball mill jar having a one-  
gallon capacity and sufficient Freon TF was added to  
cover the ceramic balls to serve as a suspension medium.  
The fibers were milled for 24 hours. Scanning electron  
10       micrographs of the milled fibers showed them to be  
broken into small fragments ranging from approximately  
2 to 10 micrometers in length.

          The milled fibers and Freon were poured into a  
shallow stainless steel pan, and the Freon was allowed  
15       to evaporate. The fibers were then dried 4 hours in an  
air-circulating oven set at 250°F (121°C) and sifted  
on a vibration plate to pass a 325 mesh screen. The  
dried, sifted fibers were stored in a desiccator box  
until ready for use.

### Composite Formation

20           The formulation S61 was prepared as follows. A  
one-gallon hot/cold pot for a Waring blender was heated  
to 140°F (60°C) using a temperature-controlled water  
25       bath. The premeasured amount of the HY906 hardener was  
put in the blender and the mixer speed was adjusted  
using a Variac variable potentiometer so that the  
hardener was just barely agitated. With the blender on  
"low" setting, the Variac was turned to 70 percent of  
30       full speed. The resin, which had been preheated to  
160°F (71°C), was added to the pot and the contents of  
the pot were mixed until the mixture appeared homogeneous  
(about 5 minutes), and then cooled to room temperature.

1 placed in an oven preheated to 275°F (135°C) and a  
thermocouple was placed on/in each of the following: on  
the mold, in the oven, and in the mold contents through  
a hole in the side wall of the mold. When the thermo-  
5 couple in the mold contents registered 275°F (135°C),  
the following cure cycle was run: 10 minutes at 275°F  
(135°C); 10 minutes at 300°F (149°C); 120 minutes at  
350°F (177°C). The maximum oven rate was used for  
changing temperatures.

10 The mold was removed from the oven and was  
disassembled, and the part was removed from the mold  
while the mold was still hot, being sure to keep the  
thermocouple embedded in the syntactic foam. The part  
was deflashed as necessary with a file. For the post-  
15 cure, the demolded part was placed in an oven preheated  
to 400°F (204°C) between 0.5 inch thick aluminum plates,  
with 2-5 kilograms weight on the top plate. When the  
thermocouple in the syntactic foam registered 400°F  
(204°C), the following post-cure cycle was run: 1 hour  
20 at 400°F (204°C); 1 hour at 425°F (218°C); 1 hour at  
450°F (232°C), and 1 hour at 475°F (246°C) Finally, the  
part was removed from the oven.

The fiber reinforced syntactic foam composite  
formed as described above was found to have the properties  
shown in Table II. With regard to Table II, the  
25 following test requirements apply:

- a. CTE was determined using a quartz  
dilatometer to measure the change in  
length as a function of temperature.
- 30 b. Specific gravity was measured using a  
pycnometer.
- c. Viscosity was measured with a Brookfield  
Viscometer.

EXAMPLE 2

This example illustrates a process for forming fiber-reinforced syntactic foam composites of various compositions in accordance with the present invention.

The components of the various formulations designated as the "RSF series" are shown in Table III. The following details regarding the specific components apply to Table III.

- a. Epoxy is a mixture of 70 parts Glyamine 135 (diglycidyl ortho toluidine) and 30 parts Glyamine 120 (tetraglycidyl methylene dianiline), both materials obtained from FIC Resins of San Francisco, California, mixed with about 115 parts nadic methyl anhydride hardener and about 0.25 parts benzyldimethylaniline accelerator.
- b. Zeeospheres 0/8 are solid glass spheres having a median diameter of 3 micrometers, available from Zeelan Industries of St. Paul, Minnesota.
- c. Carbospheres Type A are hollow carbon spheres having an average diameter of 50 micrometers, available from Versar of Springfield, Virginia.
- d. 3M A 32/2500 glass bubbles are glass microspheres having a mean diameter of 50 micrometers, a specific gravity of 0.32, and a compressive strength of 2500 psi, available from the 3M Company of Minnesota.
- e. 3M A 16/500 are glass microspheres having a mean diameter of 75 micrometers, a specific gravity of 0.16, and a compressive strength of 500 psi, available from the 3M Company.
- f. Eccospheres SI are hollow silica microspheres having a diameter of 45-125 micrometers, available from Emerson and Cuming Inc. of Canton, Massachusetts.

- a. Density was determined by pycnometer.
- b. CTE was determined using a quartz dilatometer to measure the change in length ( $\Delta l$ ) as a function of temperature.
- c. Compressive strength was determined using the American Society for Testing and Materials (ASTM) Standard No. D695.
- d. Compressive modulus was determined using ASTM D695, using crosshead speed in place of strain gauges.
- e. Uniformity was determined by visual inspection.
- f. Viscosity was measured with a Brookfield Viscometer.

#### TABLE IV

## PROPERTIES OF COMPOSITES OF FORMULATIONS OF RSF SERIES

RSF-FORMULATION	DENSITY (g/cc)	CTE (10 <sup>-6</sup> in/in/°F)	COMPRESSIVE STRENGTH (psi)*	COMPRESSIVE MODULUS (10 <sup>3</sup> psi)*	UNIFORMITY (1-10)	VISCOSITY
3	0.898	16.82	15,300	394	3.7	5
4	0.881	13.81	16,300	447	4.3	4
5	0.872	15.10	16,400	406	4.0	4
6	0.869	22.16	14,300	407	3.5	5
7	0.968	20.82	15,100	394	2.7	8
8	0.982	21.39	18,400	410	4.7	7
13	1.000	25.46	14,900	386	2.3	7
14	1.019	25.55	15,400	405	1.8	6
19	0.852	14.06	13,200	411	4.0	3
20	0.694	14.09	8,600	335	2.7	2
21	0.8561	17.02	14,000	439	3.4	3
23	0.9912	20.69	16,300	384	5.5	7
25	1.0387	30.51	19,000	423	--	6
26	1.005	21.73	15,700	395	7.3	5
28	0.982	20.10	17,100	411	6.5	5
29	1.002	20.70	17,800	393	7.6	5
31	0.888	23.90	17,800	400	6.6	8
33	0.815	23.10	13,300	343	3.9	7
34	0.824	14.59	17,500	394	4.4	6
34F	0.842	14.24	17,300	425	--	--
35	0.738	17.23	10,200	303	4.0	6
36	0.745	17.14	12,100	335	3.0	5

\* 1 psi = 1.45 x 10<sup>-4</sup> pascals

1	<u>Filler Component</u>	<u>WT. (gms.)</u>
	Carbosphere, 50 micrometers	50
	HM-S fiber, 50 micrometers	50
5	Titanate sizing agent KR238M	1

Using the above-noted resin and filler, each of a series of resin/filler formulations shown in Table V was processed as described below in order to form the composite of the present invention.

The filler composition (i.e. a mixture of the fibers and microspheres pretreated with the sizing agent as previously described herein) was loaded into a cleaned 5.5 inch x 0.5 inch (14cm x 1.3cm) wide slab mold internally coated with a polyvinyl alcohol release agent. The mold was preheated to 212°F (100°C), the temperature at which hardening of the heat curable epoxy resin formulation was initiated. The epoxy resin formulation was poured into the mold containing the filler. The mold was placed in a laminating press, a nylon vacuum bag was constructed around the compression tooling of the press, and a vacuum pressure of 125 millimeters (mm) mercury pressure (166,625 pascals) was maintained on the assembly for 2 minutes to draw down the resin to impregnate the filler and to degas the resin materials in the mold. The vacuum was then released without removal of the vacuum bag and the assembly held in this passive vacuum state for an additional 2 minutes. Thereafter, a constant positive pressure of approximately 800 pounds per square inch (41,360 mm Hg or  $5.5 \times 10^6$  pascals) was imposed on the resin/filler mixture in the mold for 2 hours at 212°F (100°C). During this pressurization stage, the resin was bled from the mold in the amount noted in Table V.

TABLE V  
COMPONENTS OF MOLDING COMPOSITION

Specimen No.	Resin (gms.)	Filler (gms.)	Filler Ratio		Resin Bleed During Molding %
			(Wt.%)	(Vol.%)	
1	40	10	45	64	69.2
2	30	9.4	38	57	47.8
3	30	9.4	38	57	47.9
4	17.0*	5.5	37	57	45.3
5	19.0*	6.0	39	59	50.6
6	20.7*	6.5	41	60	54.6

\* KR134S sizing agent was substituted for the previously noted sizing agent.

$$** \text{ Resin bleed} = \left( \frac{W_1 - W_2}{W_1} \right) 100$$

where  $W_1$  = initial resin weight

$W_2$  = resin displaced from the mold, using a bleeder cloth.

Vol. % calculated from resin bleed varies about 10-20% of the actual vol. % value.

EXAMPLE 4

This example illustrates the formation of composites as set forth in Example 3 with the exception that the composition of the filler formulation was varied. The procedure set forth in Example 3 was followed except that the filler compositions shown in Table VII were used. The following details regarding the specific components apply to Table VII.

- a. Carbospheres are carbon microspheres having a specific gravity of 0.32 and a mean diameter of 50 micrometers, available from Versar Corporation.
- b. HM-S 50 (50 $\mu$ ) graphite fibers are graphite fibers having a length of about 50 micrometers and a diameter of about 8 micrometers, available from the Courtaulds Co. of the United Kingdom.
- c. 1/4 mm HM-S 50 graphite fibers are graphite fibers having a length of about 250 micrometers and a diameter of about 8 micrometers, available from the Courtaulds Co. of the United Kingdom.
- d. C15/250 glass microballoons are composed of borosilicate glass, have a diameter of 10-200 micrometers, a density of 0.15 gm/cm<sup>3</sup>, and a compressive strength of 250 psi, available from the 3M Company of Minnesota.

The physical properties of the molded composite slabs so formed are set forth in Table VIII.

TABLE VIII

## PHYSICAL PROPERTIES OF MOLDED COMPOSITE SLABS

Filler Used in Molded Sample	Thickness (in.)	Density (gm/cm <sup>3</sup> )	Filler Ratio		Resin Bleed %	Cu Coating Removed
			(Wt.%)	(Vol.%)		
A	0.443	1.050	39	59	51.0	≤ 5%
B	0.540	0.753	26-47	56-77	61.9	≤ 5%
C	0.850	0.948	27	54	16.2	5-15%

In addition, the surfaces of the molded composite slabs of Table VIII were then subjected to plasma treatment under the following conditions: O<sub>2</sub>/inert gas source of approximately 1000 ml/minute, vacuum pressure of 200 $\mu$  Hg, and one hour duration. The surfaces of the plasma etched slabs were then copper plated to a thickness of about 3-4 mils by dipping the etched slabs in an aqueous Shipley #328 electroless copper plating bath.

The plated composite was then evaluated for adhesion of the deposited copper layer using the ASTM D3359 tape adhesion test and thermal shock cycle of Example 3. The adhesion results are recorded in Table VIII, indicating the amount of copper coating on lattice removed by the tape.

1 requirements for use in space applications. Syntactic  
foams plated with metals such as silver and copper may  
serve as metal-plated core materials for both microwave  
components and microwave reflectors.

5 The fiber-reinforced syntactic foam composites of  
the present invention achieve a 3-to-1 reduction in  
weight in comparison with aluminum, which makes these  
components attractive for weight-sensitive applications  
in a spacecraft environment. At the same time, however,  
10 in situations calling for high volume production, the  
readily-moldable nature of the reinforced foam mixture  
disclosed herein further offers the potential of signi-  
ficantly reduced cost in comparison with the machining  
traditionally employed for the production of conventional  
15 metal parts.

The preceding description has presented in detail  
exemplary preferred ways in which the concepts of the  
present invention may be applied. Those skilled in the  
art will recognize that numerous alternatives encompassing  
20 many variations may readily be employed without departing  
from the intention and scope of the invention set forth  
in the appended claims. In particular, the present  
invention is not limited to the specific resin, fibers,  
or microballoons set forth herein as examples. By  
25 following the teachings provided herein relating to the  
effect of each component of the mixture on the final  
composite and the effect of the various components on  
each other, other suitable resin, fiber, and microballoon  
materials may readily be determined. Further, by  
30 following the teachings provided herein, it may be  
determined how to form composite materials having a  
density or coefficient of thermal expansion other than  
those set forth herein as required for the specifically  
mentioned end use in space applications.

35

MEL:tp

[170-2]

1           5. The composite of Claim 3 wherein the polyfunctional curing agent is a polyamine, a polycarboxylic acid anhydride, or the maleic anhydride adduct of methyl cyclopentadiene.

1           6. The composite of Claim 3 wherein the mixture further comprises benzyldimethylaniline as an accelerator.

1           7. The composite of Claim 1 wherein the hollow microspheres are formed of glass, silica, carbon, acrylate resins, or phenolic resins.

1           8. The composite of Claim 7 wherein the hollow microspheres are formed of glass and have an average diameter of about 50 micrometers.

1           9. The composite of Claim 7 wherein the hollow microspheres comprise a mixture of glass microspheres and carbon microspheres.

1           10. The composite of Claim 1 wherein the fibers are formed of graphite, glass, carbon, nylon, or polyamide.

1           11. The composite of Claim 10 wherein the fibers are formed of graphite and have a length of about 50 micrometers and a diameter of about 8 micrometers.

1           18. The composite of Claim 16 wherein the  
polycarboxylic acid anhydride is present in sufficient  
quantity to react with from about 60 to about 90 percent  
of the epoxide groups in said polyglycidyl aromatic  
5   amine.

1           19. The composite of Claim 16 wherein the  
polycarboxylic acid anhydride is nadic methyl anhydride,  
methyl tetrahydrophthalic anhydride, or methyl  
hexahydrophthalic anhydride.

1           20. The composite of Claim 16 wherein said curing  
accelerator is present in the amount of about 0 to  
about 3 percent, by weight.

1           21. The composite of Claim 16 wherein said curing  
accelerator is 2-ethyl-4-methyl imidazole or stannous  
octoate.

1           22. The composite of Claim 16 wherein:  
a) said uncured polyglycidyl aromatic amine  
is diglycidyl orthotoluidine and is present in the  
amount of about 100 parts per hundred resin by weight;  
5           b) said curing agent is nadic methyl anhydride  
and is present in the amount of about 100 parts per  
hundred resin by weight; and  
c) said curing accelerator is 2-ethyl-4-  
methyl imidazole and is present in the amount of about  
10   2 parts per hundred resin by weight.

1           25. A fiber-reinforced syntactic foam composite  
as set forth in Claim 1, comprising:

5           a) a heat curable thermosetting epoxy  
resin comprising a mixture of tetraglycidyl methylene  
dianiline, nadic methyl anhydride, and benzyldimethyl-  
aniline;

          b) hollow glass microspheres having a mean  
diameter of about 75 micrometers; and

10           c) graphite fibers having a length of about  
150 micrometers and a diameter of about 8 micrometers.

1           26. An article of manufacture comprising a body  
formed from the composite material of Claim 1.

1           27. The article of manufacture set forth in Claim  
26 which further comprises a layer of electrically  
conductive material adhered to selected surfaces of the  
body.

1           28. The article of manufacture set forth in Claim  
27 wherein said article comprises a component in an  
antenna structure.

1           29. A method for fabricating a fiber-reinforced  
syntactic foam composite as set forth in Claims 1-25,  
which comprises the steps of:

5           a) admixing a heat curable thermosetting  
resin, hollow microspheres having a diameter in the  
range of about 5 to about 200 micrometers and fibers  
having a length less than or equal to 250 micrometers  
to form a mixture of the resin, microspheres and fibers;  
and

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/00625

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> : C 08 J 9/32; C 08 L 63/00; H 01 Q 15/14; C 08 K 7/00																							
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; text-align: left; border-bottom: 1px solid black;">Classification System</th> <th style="text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">IPC<sup>4</sup></td> <td style="vertical-align: top; padding: 5px;">C 08 J; C 08 K C 08 L; H 01 Q;</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC <sup>4</sup>	C 08 J; C 08 K C 08 L; H 01 Q;																	
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; text-align: left; padding: 5px;">Category <sup>10</sup></th> <th style="width: 70%; text-align: left; padding: 5px;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; text-align: left; padding: 5px;">Relevant to Claim No. <sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 2058794, (NITTA BERUTO) 15 April 1981, see claims; page 1, lines 53-85; examples</td> <td style="vertical-align: top; padding: 5px;">1, 2, 7, 10, 12, 26, 29</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">CA, A, 1063747 (J.D.L. TESSIER et al.) 2 October 1979, see claims 1, 4; page 4a - page 5, line 2</td> <td style="vertical-align: top; padding: 5px;">1, 2, 7, 10, 12, 26, 29</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Chemical Abstracts, Volume 89, part 2, 10 July 1978, (Columbus, Ohio, US) see abstract No. 89=7325F &amp; JP, A, 7818647 (SUMITOMO ELECTRIC IN- DUSTRIES)</td> <td style="vertical-align: top; padding: 5px;">1-3, 5, 7, 10, 12, 26, 29</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 1271298 (CIBA-GEIGY) 19 April 1972, see claims 1-8; page 2, lines 50-79; examples I, II; pages 35-124</td> <td style="vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">FR, A, 2112215 (GRUNZWEIG &amp; HARTMANN) 16 June 1972, see claims 1, 2, 4, 5</td> <td style="vertical-align: top; padding: 5px;">26, 27, 28</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0102335 (KEMANORD) 7 March 1984,</td> <td></td> </tr> </tbody> </table> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	GB, A, 2058794, (NITTA BERUTO) 15 April 1981, see claims; page 1, lines 53-85; examples	1, 2, 7, 10, 12, 26, 29	A	CA, A, 1063747 (J.D.L. TESSIER et al.) 2 October 1979, see claims 1, 4; page 4a - page 5, line 2	1, 2, 7, 10, 12, 26, 29	A	Chemical Abstracts, Volume 89, part 2, 10 July 1978, (Columbus, Ohio, US) see abstract No. 89=7325F & JP, A, 7818647 (SUMITOMO ELECTRIC IN- DUSTRIES)	1-3, 5, 7, 10, 12, 26, 29	A	GB, A, 1271298 (CIBA-GEIGY) 19 April 1972, see claims 1-8; page 2, lines 50-79; examples I, II; pages 35-124	1	A	FR, A, 2112215 (GRUNZWEIG & HARTMANN) 16 June 1972, see claims 1, 2, 4, 5	26, 27, 28	A	EP, A, 0102335 (KEMANORD) 7 March 1984,	
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<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;">           Date of the Actual Completion of the International Search  <div style="text-align: center; font-weight: bold;">1th July 1985</div> </td> <td style="width: 50%; padding: 5px; vertical-align: top;">           Date of Mailing of this International Search Report  <div style="text-align: center; font-weight: bold;">17 JUL. 1985</div> </td> </tr> <tr> <td style="padding: 5px; vertical-align: top;">           International Searching Authority  <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="padding: 5px; vertical-align: top;">           Signature of Authorized Officer  <div style="text-align: right;">               G.L.M. Kluvdenberg           </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">1th July 1985</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">17 JUL. 1985</div>	International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right;">               G.L.M. Kluvdenberg           </div>																	
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/US 85/00625 (SA 9453)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/07/85

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2058794	15/04/81	None	
CA-A- 1063747	02/10/79	SE-A- 7608086	31/01/77
GB-A- 1271298	19/04/72	DE-A, B, C 1957114	11/06/70
		FR-A- 2030072	30/10/70
		US-A- 3652486	28/03/72
FR-A- 2112215	16/06/72	NL-A- 7103795	05/04/72
EP-A- 0102335	07/03/84	SE-A- 8204595	06/02/84
		JP-A- 59047236	16/03/84
		US-A- 4483889	20/11/84